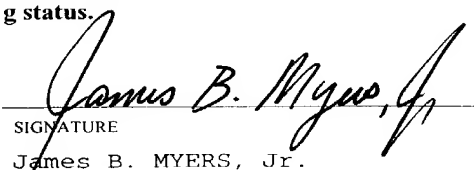


JC06 Rec'd PCT/PTO 30 JAN 2001

FORM PTO-1390 (REV 10-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 7024499PUR93	
INTERNATIONAL APPLICATION NO.: PCT/US99/17422		U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/744793	
INTERNATIONAL FILING DATE July 30, 1999		PRIORITY DATE CLAIMED July 30, 1998	
TITLE OF INVENTION LOW TEMPERATURE OXYGEN GAS SENSOR			
APPLICANT(S) FOR DO/EO/US Said MANSOUR, Mark BRAZIER, and Michael MCELFRISH			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.			
2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.			
3. <input checked="" type="checkbox"/> This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).			
4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).			
5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))			
a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).			
b. <input type="checkbox"/> has been communicated by the International Bureau.			
c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).			
6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(3)).			
7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19(35 U.S.C. 371(c)(3))			
a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).			
b. <input type="checkbox"/> have been communicated by the International Bureau.			
c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.			
d. <input checked="" type="checkbox"/> have not been made and will not be made.			
8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).			
9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). unsigned			
10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).			
Items 11 to 16 below concern document(s) or information included:			
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.			
12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.			
13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.			
<input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.			
14. <input type="checkbox"/> A substitute specification.			
15. <input type="checkbox"/> A change of power of attorney and/or address letter.			
16. <input checked="" type="checkbox"/> Other items or information:			
a. PCT Request			
b. International Publication			
c. Article 34 Amendment			
d. Written Opinion			
e. Response to Second Written Opinion			
f. PCT/IPEA/402			
g. PCT/IB/332,304,308			
h. Two (2) sets of formal drawings			

Express Mail Label No.: EL414479715US
 Date of Deposit: 30 January 2001
 I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.
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U.S. APPLICATION NO. of known, see 37 CFR 1.53 09/744793		INTERNATIONAL APPLICATION NO PCT/US99/17422		ATTORNEY'S DOCKET NUMBER 7024499PUR93		
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY		
				\$	690	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	130	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE			
Total claims	71 - 20 =	51	X \$18.00	\$	918	
Independent claims	9 - 3 =	6	X \$80.00	\$	480	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$	n/a	
TOTAL OF ABOVE CALCULATIONS =				\$	2218	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	1109	
SUBTOTAL =				\$	1109	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	n/a	
TOTAL NATIONAL FEE =				\$	1109	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	n/a	
TOTAL FEES ENCLOSED =				\$	1109	
				Amount to be refunded:	\$	
				charged:	\$	
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>1109</u> to cover the above fees is enclosed.						
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.						
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-3030</u> . A duplicate copy of this sheet is enclosed.						
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.						
SEND ALL CORRESPONDENCE TO James B. MYERS, Jr. WOODARD, EMHARDT, NAUGHTON, MORIARTY & MCNETT Bank One Center/Tower, Suite 3700 111 Monument Circle Indianapolis, Indiana 46204 US						
				 SIGNATURE James B. MYERS, Jr.		
				NAME		
				#42,021		
				REGISTRATION NUMBER		

09/744793

JC02 Rec'd PCT/PTO 30 JAN 2001

PUR-115 JBM 115798

Atty. Dkt. 7024-499

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of:)
)
Mansour Said, et al.)
)
Serial No.)
)
Filed Herewith)
)
LOW TEMPERATURE)
OXYGEN GAS SENSOR)

"Express Mail" Label No: EL414479715US
Date of Deposit 30 January 2001
I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, DC 20231-9999
Vincent Schnepel
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PRELIMINARY AMENDMENT

Hon. Commissioner for Patents
BOX PCT
Washington, D.C. 20231

Sir:

Please consider this Preliminary Amendment in the above-captioned patent application prior to examination. A copy of the amended claims with the omitted material enclosed in brackets and the added material underlined is provided on a separate sheet and attached to this Response as an Addendum. It is believed no fee is due; however, please charge any fees that may be due or credit any overpayment to Deposit Account No. 23-3030, but not to include payment of any issues fees which are or may become due.

IN THE CLAIMS

Please amend the following claims:

3. (Amended) The apparatus of claim 1 having an effective operating temperature below about 375K.

4. (Amended) The apparatus of claim 1 having an effective operating temperature below about 300K.
5. (Amended) The apparatus of claim 1, wherein said sensor includes at least two metallic electrodes.
7. (Amended) The apparatus of claim 1 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.
9. (Amended) The apparatus of claim 2, wherein said gradient is established by a number of differently composed layers.
10. (Amended) The apparatus of claim 1, wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
15. (Amended) The apparatus of claim 1, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.
17. (Amended) A method of detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 1.

18. (Amended) A method of manufacturing an oxygen sensing device, said method, comprising:
- providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;
 - irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and
 - forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.
22. (Amended) The method of claim 18 further comprising performing said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.
23. (Amended) The method of claim 18, wherein said irradiating includes scanning a predetermined path along the source with the laser.
25. (Amended) The method of claim 18, wherein said forming includes depositing the mixture on a substrate.
26. (Amended) An oxygen sensor formed by the method of claim 18.
31. (Amended) The method of claim 27, wherein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.
32. (Amended) The method of claim 27, wherein said irradiating includes scanning across a predetermined path along the source with a laser.
34. (Amended) The method of claim 27, wherein said forming includes depositing material from a first one of the plumes on a substrate.

35. (Amended) An oxygen sensor formed by the method of claim 27.
41. (Amended) The apparatus of claim 36, wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.
43. (Amended) The apparatus of claim 41, wherein said two compositional constituents are zirconia and titania.
44. (Amended) The apparatus of claim 36 wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
46. (Amended) A method of detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 36.
49. (Amended) The combination of claim 47, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm .
51. (Amended) The combination of claim 47, wherein said sensing member is comprised of a ferroelectric material.
52. (Amended) The combination of claim 47, wherein said sensing member is comprised of a PZT material.
53. (Amended) The combination of claim 47, wherein the system is operable to detect oxygen concentration at a temperature below about 400K.

Please add new claims 54-71 as follows:

54. (Added) The apparatus of claim 2 having an effective operating temperature below about 375K.

55. (Added) The apparatus of claim 2 having an effective operating temperature below about 300K.

56. (Added) The apparatus of claim 2, wherein said sensor includes at least two metallic electrodes.

57. (Added) The apparatus of claim 2 and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

58. (Added) The apparatus of claim 2, wherein said at least two compositional constituents are zirconia and titania.

59. (Added) The apparatus of claim 8, wherein said gradient is established by a number of differently composed layers.

60. (Added) The apparatus of claim 2, wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.

61. (Added) The apparatus of claim 60, wherein x increases along a direction through said sensing member and y decreases along said direction.

62. (Added) The apparatus of claim 61, wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.

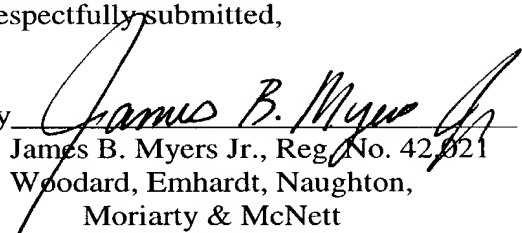
63. (Added) The apparatus of claim 60, wherein said sensing member includes a number of layers each having a different ratio of x to y.
64. (Added) The apparatus of claim 60, wherein x is about 0.55 and y is about 0.45 along a first surface of said sensing member and x is about 0.75 and y is about 0.25 along a second surface of said sensing member opposite said first surface.
65. (Added) The apparatus of claim 2, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.
66. (Added) The apparatus of claim 65 wherein the said sensing member is comprised of a YSZ material.
67. (Added) The combination of claim 48, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm .
68. (Added) The combination of claim 67, wherein said peak magnitude is in a range of about 10 volts per μm to about 100 volts per μm .
69. (Added) The combination of claim 48 wherein said sensing member is comprised of a ferroelectric material.
70. (Added) The combination of claim 48, wherein said sensing member is comprised of a PZT material.
71. (Added) The combination of claim 48, wherein the system is operable to detect oxygen concentration at a temperature below about 400K.

REMARKS

Entry of this Preliminary Amendment prior to the examination of this application is respectfully requested. Claims 54-71 have been added by this amendment, and the accompanying filing fee is based on the status of the claims after entry of this Amendment. Applicants respectfully request consideration of this application and Preliminary Amendment, and passage of this application to allowance.

Respectfully submitted,

By


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ADDENDUM

3. (Amended) The apparatus of claim 1 [or 2] having an effective operating temperature below about 375K.
4. (Amended) The apparatus of claim 1 [or 2] having an effective operating temperature below about 300K.
5. (Amended) The apparatus of claim 1 [or 2], wherein said sensor includes at least two metallic electrodes.
7. (Amended) 7. The apparatus of claim 1 [or 2] and further comprising a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.
9. (Amended) The apparatus of claim 2 [or 8], wherein said gradient is established by a number of differently composed layers.
10. (Amended) The apparatus of [any of claims] claim 1 [or 2], wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
15. (Amended) The apparatus of claim 1 [or 2], wherein said sensing member is comprised of an oxygen deficient ionic oxide material.
17. (Amended) A method of [use, comprising] detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 1 [or 2].

18. (Amended) A method of [manufacture] manufacturing an oxygen sensing device, said method, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and

forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.

22. (Amended) The method of [any of claims] claim 18[-21] further comprising performing said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.

23. (Amended) The method of [any of claims] claim 18[-21], wherein said irradiating includes scanning a predetermined path along the source with the laser.

25. (Amended) The method of [any of claims] claim 18[-21], wherein said forming includes depositing the mixture on a substrate.

26. (Amended) An oxygen sensor formed by the method of [any of claims] claim 18[-21].

31. (Amended) The method of [any of claims] claim 27[-30], wherein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.

32. (Amended) The method of [any of claims] claim 27[-30], wherein said irradiating includes scanning across a predetermined path along the source with a laser.

34. (Amended) The method of [any of claims] claim 27[-30], wherein said forming includes depositing material from a first one of the plumes on a substrate.
35. (Amended) An oxygen sensor formed by the method of [any of claims] claim 27[-30].
41. (Amended) The apparatus of [any of claims] claim 36[-40], wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.
43. (Amended) The apparatus of claim 41 [or 42], wherein said two compositional constituents are zirconia and titania.
44. (Amended) The apparatus of [any of claims] claim 36[-40] wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
46. (Amended) A method of [use, comprising] detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of [any of claims] claim 36[-40].
49. (Amended) The combination of claim 47 [or 48], wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm .
51. (Amended) The combination of claim 47 [or 48] wherein said sensing member is comprised of a ferroelectric material.
52. (Amended) The combination of claim 47 [or 48], wherein said sensing member is comprised of a PZT material.
53. (Amended) The combination of claim 47 [or 48], wherein the system is operable to detect oxygen concentration at a temperature below about 400K.

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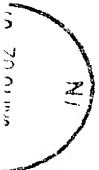
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LOW TEMPERATURE OXYGEN GAS SENSOR

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GOVERNMENT RIGHTS CLAUSE

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license to others on reasonable terms as provided for by the terms of DOE Grant No. DE-FG02-90ER45427.

10

REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application Nos. 60/094,721 filed on July 30, 1998 and 60/123,819 filed on March 11, 1999, which are both hereby incorporated by reference in their entirety.

15

BACKGROUND

20

The present invention relates to sensing devices and the manufacture thereof, and more particularly, but not exclusively, relates to a ferroelectric oxygen gas sensor and a process for manufacturing ferroelectric devices.

25

Oxygen gas sensors have a wide range of applications in combustion engine and metallurgical processes. The most notable is their use in modern automobile engine operation and control. The sensor measures the oxygen content in the exhaust of the internal combustion engine and adjusts the air-fuel ratio, accordingly. This regulation process has been found to significantly enhance economical operation and environmental control of combustion engines.

30

Two types of oxygen sensors are commonly used in the auto industry: the potentiometric type, using zirconia based ceramics such as cubic-stabilized zirconia (CSZ) and the resistive type, using titania (TiO_2). A CSZ potentiometer type sensor requires a porous metal electrode and a reference gas at the reference electrode. A high emf develops across the electrodes as the oxygen partial pressure at the sensing electrode varies or changes in comparison to the reference gas at the reference electrode. Furthermore, the sensing mechanism is a thermally activated process, which requires that the sensor be operated at a temperature higher than 300°C in order to register a significant output voltage. This is usually accomplished by positioning the sensor in a hot exhaust gas stream or by heating the sensor using an electric heater. Resistive titania sensors, on the other hand, do not require a reference gas, but do require a tip temperature $\geq 350^\circ\text{C}$ for sensor activation. Titania sensors also exhibit strong temperature dependence and require compensation for temperature variations.

Other types of solid-state oxygen sensors using LaF_3 and nonstoichiometric perovskite thin films have recently been reported. Unlike CSZ and TiO_2 sensors, the LaF_3 sensors operate at ambient temperatures, but they suffer from very long response times. Shorter response times of a few minutes were reported by operating the LaF_3 thin films at higher temperatures or by using a special type of a sensitive electroding material such as metal phthalocyanine. Sensing capabilities of non-stoichiometric perovskite thin films only appear to have been reported at higher activation temperatures for sensor activation. Thus, the need to develop a low temperature oxygen sensor with a fast response time remains. Furthermore, a low temperature sensor will have a great advantage in a wide variety of applications including medical (life support), biological and environmental applications and process monitoring.

The present invention meets such needs, and has other benefits and advantages.

SUMMARY OF INVENTION

The present invention relates to sensing devices, the manufacture and use thereof. Various aspects of the invention are novel, nonobvious, and provide various advantages. While the actual nature of the invention covered herein can only be determined with reference to the claims appended hereto, certain forms and features, which are characteristic of the preferred embodiments disclosed herein, are described briefly as follows.

One form of the present includes an oxygen sensor having an operating temperature preferably below about 400K. The temperature is more preferably below about 375K and still more preferably below about 300K. The oxygen sensor includes a nonstoichiometric metal oxide sensor member. Preferably the nonstoichiometric sensing member includes an ionic conductor such as a PZT compound or a yttria stabilized zirconia compound (YSZ).

In another form, the invention includes an oxygen sensor having a graded ferroelectric sensing member. The sensing member may be composed of a $\text{PbZr}_x\text{Ti}_y\text{O}_3$ (PZT) compound, where the ratio of x to y varies in accordance with a predetermined compositional gradient through the sensing member, and the sum of $x + y$ is generally about one. For this type of ferroelectric material, preferably x is in a range of about 0.5 to 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in a range of about 0.55 to about 0.75, and y is in a range of about 0.25 to about 0.45. Instead of PZT, other ferroelectric materials may be utilized in accordance with the present invention, such as $(\text{Ba}, \text{Sr})\text{TiO}_3$ (BST), BaTiO_3 , lanthanum-modified PZT (PLZT), and strontium bismuth tantalate (SBT) to name a few.

In another form, the present invention includes an oxygen sensor having a non-graded ferroelectric sensing member. The sensing member can be composed of a $\text{PbZr}_x\text{Ti}_y\text{O}_3$ (PZT) compound wherein the sum of x and y is generally about one. Preferably, x is in the range of about 0.5 to

about 0.8, and y is in a range of about 0.2 to about 0.5. More preferably, x is in the range of about 0.55 to about 0.75, and y is in the range of about 0.25 to about 0.45. Similar to the graded ferroelectric sensing member above, PZT can be substituted with other ferroelectric materials.

5 The ferroelectric sensing member can include electrodes formed from any suitable material including, but not limited to platinum, silver, gold, metal phthalocyanine, and metal conductive oxides such as indium-doped tin oxide (ITO) to name a few. The electrodes can be formed using conventional patterning techniques.

10 Another form of the invention includes an oxygen sensing system. This system may be configured to measure oxygen levels in an intake and/or exhaust stream of a vehicle.

 In still another form of the invention, a manufacturing technique includes: (a) providing a source of ferroelectric material having a first
15 region with a first composition and a second region with a second composition different from the first composition; (b) irradiating a portion of the first region and a portion of the second region with a laser beam to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and (c) forming a layer of a
20 sensing matrix corresponding to the ratio. Irradiation of the source may be performed by scanning a predetermined path along the source with the laser beam to generate one or more plumes of the first and second compositions. Moreover, different amounts of the first and second regions may be scanned in this manner to vary the composition of one or more
25 such plumes. Material released from the source may be accumulated in one or more layers to provide a corresponding ferroelectric device.

 In a further form, the present invention includes a nonstoichiometric metal oxide sensing member to detect oxygen and a circuit electrically coupled to said sensing member operable to apply an electric field to said
30 sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member

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may be of a time varying form, with a peak magnitude of at least about 1 volt per μm .

5 Still a further form of the present invention includes: providing a nonstoichiometric metal oxide sensing member; applying an electric field to said sensing member; and sensing oxygen with said sensing member. The sensing member may be comprised of a ferroelectric material such as a PZT or another type of nonstoichiometric metal oxide such as YSZ. The electric field applied to the sensing member may be of a time varying form with a peak magnitude of at least about 1 volt per μm .

10 Accordingly, it is one object of the present invention to provide a low temperature oxygen sensing device.

It is another object of the present invention to provide a ferroelectric device.

15 It is still another object to provide a technique to manufacture a ferroelectric device.

Further objects, features, forms, aspects, advantages, and benefits of the present invention will become apparent from the description and drawings provided herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an exhaust gas stream sensor system.

5 Figure 2 is a diagram of a vehicle employing one embodiment of an oxygen sensor in an intake gas stream sensor system.

Figure 3 is a perspective view of a sensing device according to one embodiment of the present invention.

10 Figure 4 is a diagrammatic illustration of one method for depositing a graded ferroelectric material on a substrate.

Figure 5 is a graphical illustration of an Auger depth profile of relative Zr and Ti concentrations for a down-graded film prepared according to the method depicted in Figure 4.

15 Figure 6 is a graphical illustration of (200) peaks as a function of 2θ obtained from x-ray diffraction analysis of PZT 55/45, PZT 75/25 and compositionally graded PZT films.

Figure 7 is a schematic of a Sawyer-Tower circuit coupled to an oscilloscope.

20 Figure 8 is a diagram of an atmosphere and temperature controlled probe station including a specimen stage for analyzing an oxygen sensor prepared according to the method depicted in Figure 4.

Figure 9a is a graphical illustration of the time dependence of the voltage offset for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

25 Figure 9b is a graph plotting voltage offset as a function of an applied sinusoidal driving field for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

30 Figure 10a is a graph plotting voltage offset as a function of oxygen concentration for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10b is a graph plotting voltage offset as a function of oxygen pressure for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 10c is a graph plotting voltage offset as a function of
5 temperature for one embodiment of an oxygen sensor having a non-graded ferroelectric film of the present invention.

Figure 11a is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one
10 embodiment of an oxygen sensor having an up-graded ferroelectric film of the present invention.

Figure 11b is a graph plotting voltage offset as a series of hysteresis loops as a function of an applied sinusoidal driving field for one
embodiment of an oxygen sensor having a down-graded ferroelectric film of the present invention.

Figure 12 is a graph plotting voltage offset as a function of the log of
15 oxygen pressure for an oxygen sensor having an up-graded ferroelectric film and an oxygen sensor having a down-graded ferroelectric film, which were prepared in accordance with this invention.

Figure 13 is a graph plotting the voltage offset as a function of
20 temperature for one embodiment of an oxygen sensor having an up-graded film of the present invention.

Figure 14 is a graph plotting voltage offset as a function of
Log[pO₂/atm] of a YSZ film prepared according to the present invention.

Figure 15 is a graph plotting voltage offset as a function of the
25 applied sinusoidal driving frequency for a YSZ film prepared according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described device and methods, and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates.

One embodiment of the present invention is an oxygen sensor having a variety of uses, most notably for use in sensing systems for combustion engines to measure the oxygen levels in an exhaust gas stream and/or an intake gas stream. This oxygen sensor comprises a sensing member made of either a graded or non-graded ferroelectric or other nonstoichiometric metal oxide. At least two electrodes are attached to the sensing member in spaced a part relationship from one another to provide a sensing device akin to a capacitor. When the resulting capacitor device is subjected to an applied electrical driving field, the capacitor exhibits a voltage offset under selected conditions. The magnitude of the voltage offset is dependent upon the gaseous oxygen concentration to which the device is exposed.

Oxygen sensors of the present invention can be used to enhance the efficient operation and environment or pollution control of combustion engines. Figure 1 is a diagram of a vehicle 10 having a combustion engine 12 employing sensing system 14. Sensing system 14 includes oxygen sensor 18 positioned in exhaust line 16 and operably coupled to control circuit 20. Circuit 20 may include a means to provide a driving electric field for application to sensor 18 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in exhaust gas flowing through exhaust line 16, oxygen sensor 18 provides an oxygen

signal to control circuit 20. And in response to the oxygen signal input, control circuit 20 generates one or more signals to control or adjust the operation of engine 12, which adjustments can include adjusting the fuel/air mixture into engine 12.

5 An oxygen sensor prepared as described herein can also be used in the intake gas stream of a vehicle. Figure 2 is a diagram of a vehicle 40 having a combustion engine 42 employing a sensing system 44. Sensing system 44 includes oxygen sensor 46 positioned in air intake line 48. Oxygen sensor 46 is operably coupled to control circuit 50. Circuit 50 may
10 include a means to provide a driving electric field for application to sensor 46 to generate a voltage offset corresponding to oxygen level. Such driving means are more fully discussed hereinafter in connection with Figure 7. In response to a level of oxygen in the intake gas stream flowing through air intake line 48, oxygen sensor 46 provides an oxygen signal to control
15 circuit 50. Control circuit 50 is responsive to one or more inputs and generates an output signal to control or adjust the operation of engine 42.

 When used with combustion engines the inventive oxygen sensor responds to small variations in oxygen levels in the monitored gas stream with sufficient time response and sensitivity to enhance the control and
20 operation of the combustion engine. Furthermore, the sensors function in both heated and non-heated environments for effective sensing of oxygen levels. The sensor can function in non-heated environments, for example, in non-heated intake gas streams and in exhaust gas streams upon initial start up of the engine before the exhaust gas becomes heated. Therefore,
25 the sensors can be used to enhance the control and operation of an engine upon initial startup. Control of engines upon initial start provides particular advantages because that is when the engine operates least efficiently and produces the most pollutants.

 It will be understood by those skilled in the art that the sensing
30 systems 14 and 44 including a nonstoichiometric metal oxide electrolyte and driving means prepared according to this invention will have a wide variety of applications besides use with combustion engines, for example,

WO 00/07001

PCT/US99/17422

but not restricted to, life support systems, medical (life support), biological and environmental analysis and process monitoring.

Figure 3 depicts one embodiment of a sensor member 60 prepared according to the present invention. Sensor member 60 includes sensing member 62 deposited on an electrode material 64 formed on substrate 66. A top electrode 68 is formed on sensing member 62. It will be understood by those skilled in the art that a plurality of top electrodes 68 can be formed on sensing member 62. A plurality of electrodes 68 can be coupled to a driving means to enhance detection of the offset voltage with sensor 60 as will be discussed further in connection with Figure 7. The material comprising sensing member 62 can be made of a nonstoichiometric metal oxide material that is operable as a solid-state electrolyte positioned between metal electrodes in the form of a capacitor or an electrochemical cell. Sensing member 62 may be in the form of a thin film that can be grown using controllable film deposition techniques, such as a metallo-organic deposition (MOD) spin-on, PVD (i.e., sputtering or pulsed laser deposition (PLD)), chemical vapor deposition (CVD), or MOCVD.

Figure 4 is a diagrammatic illustration of one method for depositing a graded material 80 on a substrate 82 using PLD. Source target 84 is formed of first region 86 and second region 88. First region 86 includes a first material having a first composition, and second region 88 includes a second material having a second composition different from the first composition. Regions 86, 88 meet at interface 87 which is generally positioned at about a 45° angle relative to vertical axis 92 for the illustrated embodiment. Laser 90 rasters laser beam 91 over surface 94 of source target 86 along path 96 in a boustrophedonic pattern as illustrated. As laser beam 91 scans across target 84, it liberates material from the respective region 86, 88 in the form of a plume 97 that is subsequently at least partially deposited on substrate 82 as graded material 80. It should be appreciated that for each generally horizontal scan of laser beam 91 across target 84, a different amount of material is released from region 86 relative to the amount of material released from region 88 for the illustrated

WO 00/07001

PCT/US99/17422

orientation of interface 87. Correspondingly, material 80 is formed of layers that gradually change in composition relative to the ratio of region 86 material to region 88 material. The temperature of material 80 may be maintained at a level sufficient to promote diffusion for a given layer
5 resulting in a generally homogeneous composition for that layer.

In an alternative embodiment, interface 87 may be differently configured to adjust the ratio for a given scan of laser beam 91 thereacross. Further, in other embodiments, the source target 84 may include more than two differently composed regions to be scanned to
10 provide for other types of compositions.

This deposition process was used in one example to deposit a graded ferroelectric sensing film on a Pt-Ti-SiO₂-Si substrate held at 600°C in 300 mTorr of O₂. The film has been found to be highly (111)-oriented, as determined by x-ray diffraction. For this example, the deposition process
15 employed a source with regions 86 and 88 having the ferroelectric composition of PbZr_{0.75}Ti_{0.25}O₃, PZT (75/25); and PbZr_{0.55}Ti_{0.45}O₃, PZT (55/45), respectively. Regions 86 and 88 were placed adjacent to one another with the interface at a 45° angle to vertical axis 92. A laser beam was then rastered across the target horizontally while its vertical position
20 was incrementally increased after each horizontal scan as shown by path 96. For each horizontal scan that the laser beam contacted the first and second regions of the target 84, either the first or second composition or both were deposited on substrate 82. Initially, a layer of PZT (55/45) was deposited on substrate 82. During the next scan, the laser beam released
25 an amount of PZT (75/25) as well as an amount of PZT (55/45) from the target source. The relative amounts of PZT 75/25 and PZT 55/45 released from the target for each horizontal scan and deposited on the substrate were substantially equivalent to the amount of each region, 86 and 88, scanned by the laser beam. With each successive scan, the amount of
30 PZT (55/45) deposited became less, while the amount of PZT (75/25) deposited became greater, ending with a final layer of PZT (75/25). For

this example, a total of 15 horizontal scans on the target were performed resulting in a film having a thickness of about 0.3 μm .

For convenience, films with Zr/Ti ratios varying from PZT (75/25) at the substrate to PZT (55/45) at the top surface will be referred to as "up-graded" films. Films with the opposite gradient, i.e. with Zr/Ti ratios varying from PZT (55/45) at the substrate to PZT (75/25) at the top surface, will hereafter be referred to as "down-graded" films. Using the method described above both up-graded and down-graded films can be deposited on substrates.

Both graded and non-graded sensors contain electrodes. A first or "bottom" electrode is formed on the substrate with a small section of the substrate is masked off during deposition to allow access to the bottom electrode. A second or top electrode, is formed via photolithography and sputtering or any other patterning techniques according to procedures well known to those skilled in the art. Materials useful as electrodes, including, for example, platinum, silver, gold, metal phthalocyanine and other conductive metal oxides such as indium-doped tin oxides (ITO) can be used to prepare electrodes. In one example, this second electrode was provided in the form of a number of 50 μm x 50 μm platinum pads. For this example, the resulting sensing structure was like that shown in Figure 3 except for the presence of multiple top electrode pads.

In this manner a compositionally graded sensor element can be prepared at a temperature sufficiently low to be suitable for silicon-based substrates. Correspondingly, processing techniques developed for silicon substrates for use in other applications, such as semiconductor microstructures, may be utilized. The method also obviates the need to interdiffuse successively applied layers each having a compositionally different ferroelectric material.

The relative Zr/Ti concentration of the gradient films as a function of depth is determined using a combination of Auger electron spectroscopy and ion milling to construct a depth profile. X-ray diffraction was used to determine crystalline structure and orientation of the films.

Figure 5 shows the results of Auger depth profiling. The resulting plot is the relative concentration of Zr and Ti as a function of depth for a typical down-graded film prepared as described in connection with Figure 4. The depth profile indicates that the deposition method produces smooth,
5 linear composition gradients, either from PZT (75/25) to PZT (55/45), or vice versa. X-ray diffraction measurements are also consistent with the presence of a range of compositions in the films rather than discrete layers of PZT (55/45) and PZT (75/25).

Figure 6 is a plot of the x-ray diffraction measurements of the (200)
10 peak of an up-graded film prepared as described in connection with Figure 4 along with the (200) peaks for non-graded Zr/Ti 55/45 and Zr/Ti 75/25 films. It is known that the positions of the x-ray peaks for PZT shift with composition. This is evidenced by the two distinct peaks from 55/45 at $2\theta = 44.65^\circ$ and 75/25 at $2\theta = 44.15^\circ$. The peak from the graded film,
15 however, is broad and centered at $2\theta = 44.45^\circ$, which is consistent with a film having a range of compositions between PZT (55/45) and PZT (75/25). Naturally, in other embodiments, oxygen sensors in accordance with the present invention may be manufactured using other processes and techniques as would occur to those skilled in the art.

Figure 7 depicts a schematic of a Sawyer-Tower circuit 110 coupled
20 to an oscilloscope 112. Circuit 110 includes an electrical energy source 114 in the form of a variable voltage supply that generates a frequency adjustable time varying voltage, preferably sinusoidal in nature. Circuit 110 includes a nonstoichiometric metal oxide sensor of the present invention
25 such as a ferroelectric PZT or other type, which is schematically represented as sensor capacitor 115 (C_s). Circuit 110 also includes reference capacitor 117 (C_{ref}) in series with capacitor 115. The time varying voltage from source 114 is applied across the series of capacitors 115, 117, providing a corresponding periodic time varying electric field to
30 drive capacitor 115. The electric field has a peak amplitude or magnitude of at least 1 volt per μm . The peak magnitude of the electric field is more preferably in a range of about 1 to about 1000 volts per μm , and still more

preferably is in a range of about 10 to about 100 volts per μm . A most preferred range of the electric field is about 20 to about 50 volts per μm peak to peak amplitude.

A sinusoidal driving electric field applied to sensor capacitor 115 by circuit 110 generates a hysteretic polarization and an offset voltage. The driving voltage (E_{drive}) generated by source 114 is connected to the x-input of oscilloscope 112 while the voltage across the reference capacitor 117 (C_{ref}) is amplified by amplifier 116 and connected to the y-input of oscilloscope 112. In an ideal system the polarization on the sensor capacitor C_s is proportional to the voltage on the reference capacitor (i.e., sample charge, Q , is equal to the reference capacitor charge, Q_{ref}). In graded and non-graded films, however, a voltage develops across the film leading to voltage across the sensor capacitor 115 (C_s) that is equal and opposite to the voltage across the reference capacitor 117 (C_{ref}).

Circuit 110 was utilized to test the response of various PZT materials with non-graded or graded structures to various mixtures of N_2 and O_2 gases. This response was measured as offset voltage vs. time, t . The ambient oxygen partial pressure, $p(\text{O}_2)$, was controlled via two mass-flow controllers that determined the ratio of N_2 , (or Ar gas) and O_2 entering the chamber. Each particular gas mixture was allowed to flow through the chamber for one hour, at which point a driving electric field at 1 KHz was applied. The subsequent offset voltage was measured as a function of time. This was done using the following N_2/O_2 ratios: (100/0); (95/5); (90/10); (80/20); (50/50); and (0/100).

Reported measurements were performed using a specimen stage comprised of an atmosphere and temperature controlled probe station to allow voltage measurements at ambient temperature. Figure 8 is a diagram of a atmosphere and temperature controlled probe station including sample stage 152 that is a combination resistive heater and Joule-Thompson refrigerator enclosed within sealed housing 154. Sensor 153 is positioned on sample stage 152. Housing 154 includes inlet ports 156 and 158 and exit ports 160 and 162. Oxygen from source 164 flows

WO 00/07001

PCT/US99/17422

through line 166 into mass flow controller 168 and then through line 170 to inlet port 158 of housing 154. Nitrogen from source 172 flows through line 174 into mass flow controller 176 and then through line 178 into inlet port 156 of housing 154. Exit port 160 is connected to a vacuum pump (not shown), and exit port 162 is connected to a bypass valve (not shown). Probes 180 and 182 connect an oxygen sensor to the power supply of the Sawyer-Tower circuit (not shown) inside probe station 150. The system includes two mass flow controllers, 168 and 176, which regulate the flow of different gases from sources 164 and 172 into station 150. The mass-flow controllers were calibrated using a commercial zirconia oxygen sensor. In one operation mode to allow voltage measurements at ambient pressure, the gases in station 150 flow out exit port 162 through a bypass valve (not shown). In alternative operation modes at reduced pressure, exit port 162 is closed and gases inside station 150 are removed through exit port 160 using a vacuum pump or other vacuum source to provide a partial vacuum in station 150. In yet another operation mode, an oxygen sensor is mounted on a stage 152 that is a combination of a resistive heater and a Joule-Thompson refrigerator. This allows measurements to be performed at temperatures from 77K to 580K.

Figure 9a is a plot of the voltage offset as a function of time for a non-graded ferroelectric film. The time dependence of the voltage offset, $V_{\text{off}}(t)$ has the characteristic shape of a capacitor charging up through a resistance. By varying 117 (C_{ref}) and the amplifier 116 in the Sawyer-Tower circuit, it was determined that the time constant, τ , for the time dependence of V_{off} is approximately equal to $C_{\text{ref}}R_{\text{in}} = 10$ s. Voltage offsets with this type of time dependent behavior measured using the Sawyer-Tower circuit have previously been shown to be a direct result of an equal and opposite voltage that develops on the sample capacitor. Furthermore, the voltage offset develops only when the driving field is applied, the effect is not observed when the applied field is zero. Figure 9b shows the driving field, E_{drive} , dependence of voltage offset, V_{off} . Below a field, E_{min} , V_{off}

increases monotonically with the driving field. Above E_{\min} , V_{off} displays a power law dependence on the driving field.

Figure 10a shows the offset voltage as a function of oxygen concentration measured in various combinations of O_2 and N_2 gas at room temperature using a 1 kHz, to 50 V/ μm driving field for a non-graded PZT film. A strong dependence of voltage offset on oxygen partial pressure is observed. Figure 10b shows the offset voltage as a function of the oxygen pressure inside the probe station 150 after it was flushed with oxygen gas and pressurized with oxygen at varying absolute pressures. In both cases the magnitude of offset voltage translates to lower d.c. voltage values as the oxygen pressure decreases. The magnitude of V_{off} increases dramatically as the ambient pO_2 is reduced.

Figure 10c shows the voltage offset as a function of temperature. The voltage offset persists over a wide range of temperatures. In preferred embodiments, a non-graded PZT film develops a d.c. voltage offset when subjected to a sinusoidal driving field over a temperature range from about 180K to about 450K for a non-graded PZT film. Correspondingly, the non-graded PZT film for this example has an effective operating range that at least extends between about 180K and about 450K. More preferably for this example, the non-graded PZT film has an effective operating range at least between about 180K and about 400K; and still more preferably between about 180K and about 375K; where effective operating range is understood to mean that the film provides a significant, measurable d.c. voltage offset in response to an applied electric driving field.

In another form, the present invention includes a compositionally graded ferroelectric device prepared according to the method depicted in Figure 4. The compositionally graded ferroelectric devices exhibited similar characteristics under the influence of a periodically time varying driving electric field. The compositionally graded PZT film develops a d.c. voltage offset under the influence of the field. Figure 11a is a graph plotting the d.c. voltage offset observed as a series of hysteresis loops as a function of the applied sinusoidal driving field for an up-graded PZT film. Figure 11b is

a corresponding plot for the down-graded film. The direction of the voltage offset depends on the direction of the gradient with respect to the substrate. For the up-graded film, application of a non-zero driving field provide hysteresis loops that reach an equilibrium offset after a few seconds. The hysteresis loops for the up-graded film translate in a positive d.c. voltage direction while those for the down-graded film translate in a negative d.c. voltage direction when the applied sinusoidal driving field is increased. The hysteresis loops measurements were made using the Sawyer-Tower circuit depicted in Figure 7 using a 1 kHz driving field that was varied from zero to 50 V/ μ m.

Compositionally graded devices exhibit results similar to those observed for non-graded devices when subjected to various combinations of O₂ and N₂ gas at room temperature and a 1 kHz, 30 V/ μ m driving field for the up-graded films. Figure 12 shows the relationship between the offset voltage as a function of Log[pO₂/atm] with a driving field of 1 kHz, 35 V/ μ m at 300K for up-graded and down-graded films. The plot indicates that the magnitude of the voltage offset depends on the ambient oxygen partial pressure. The offset voltage monotonically increased as the oxygen pressure in the chamber increased.

Figure 13 shows the offset voltage as a function of temperature for an up-graded PZT thin film in the temperature range 300K < T < 400K. Offset voltage was observed to monotonically increase as the temperature increased. Furthermore, a significant response was detected at ambient and sub-ambient temperatures. The voltage offset for a graded PZT film persists over a wide range of temperatures. The d.c. voltage offset for a graded PZT film can be observed as low as 400K, or 375K, and even as low as 300K or lower. Thus the graded PZT film may preferably be used for sensing at temperatures below about 400K. More preferably, sensing may be in a range between about 300K and about 400K.

In yet another form, the inventive oxygen sensor includes an oxygen deficient ionic oxide material. One example of an oxygen deficient ionic oxide is yttria stabilized zirconia (YSZ). In one example, the YSZ films

were fabricated using pulsed laser deposition on Pt-Ti-SiO₂-Si substrates held at 600 °C in 50 mTorr of O₂. The YSZ material has the composition of Y_xZr_{1-x}O₂, where x is in the range of 0.0 to 0.15. In a preferred form, YSZ film has the composition of Y_{0.06}Zr_{0.94}O₂. The YSZ films were prepared to be approximately 0.8 μm thick and preferentially (111)-oriented as determined by x-ray diffraction.

Figure 14 shows the results of the measurement of V_{off} at 300 K in different pO₂ environments with an applied electric field of 19 V/μm at 100 kHz. For atmospheres of Log[pO₂/atm] ~ 0 to -1, a small (~ 0.1 mV) positive voltage offset was observed which decreased with decreasing pO₂. As Log[pO₂/atm] was reduced below ~ -0.5, an increasingly negative voltage offset was observed with the largest magnitude of ~ -1.4 mV occurring at Log[pO₂/atm] ~ -3, the lowest pO₂ value tested in this example.

Figure 15 is a graph plotting -V_{off} as a function of the driving frequency and shows the frequency response of a typical sample capacitor driven with a 19 V/μm applied field in an atmosphere of Log[pO₂/atm] ~ -3. The maximum response was observed to occur at a driving frequency of approximately 300 kHz. The magnitude of the voltage offset also increased exponentially with the amplitude of the applied electric field.

Correspondingly, the YSZ film can be used at temperatures below about 300K to sense oxygen. The resulting sensor may be quite small, and it requires no reference gas, making it suitable for biomedical applications (among others).

Any publications, patents, or patent applications cited herein are hereby incorporated by reference as if each publication, patent or patent application were set forth in its entirety herein. The citations incorporated by reference include the following:

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to

WO 00/07001

PCT/US99/17422

be protected. Further, any theory of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to make the scope of the present invention dependent upon such theory, proof, or finding.

CLAIMS

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- 20

8. The apparatus of claim 2, wherein said at least two compositional constituents are zirconia and titania.
9. The apparatus of claim 2 or 8, wherein said gradient is established
5 by a number of differently composed layers.
10. The apparatus of any of claims 1 or 2, wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
10
11. The apparatus of claim 10, wherein x increases along a direction through said sensing member and y decreases along said direction.
12. The apparatus of claim 11, wherein x is in a range of about 0.55 to
15 about 0.75 and y is in a range of about 0.25 to about 0.45.
13. The apparatus of claim 10, wherein said sensing member includes a number of layers each having a different ratio of x to y.
- 20 14. The apparatus of claim 10, wherein x is about 0.55 and y is about 0.45 along a first surface of said sensing member and x is about 0.75 and y is about 0.25 along a second surface of said sensing member opposite said first surface.
- 25 15. The apparatus of claim 1 or 2, wherein said sensing member is comprised of an oxygen deficient ionic oxide material.
16. The apparatus of claim 15 wherein the said sensing member is comprised of a YSZ material.
30
17. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of claim 1 or 2.

18. A method of manufacture, comprising:

providing a source of ferroelectric material having a first region with a first composition and a second region with a second composition different from the first composition;

5 irradiating a portion of the first region and a portion of the second region with a laser to release a mixture from the source with a predetermined ratio of the first composition to the second composition; and forming a layer of a sensing matrix from the mixture, the mixture corresponding to the ratio.

10

19. The method of claim 18, wherein said source is a solid composed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x and y have a first predetermined ratio in the first region and a second predetermined ratio in the second region, the first predetermined ratio being different from the second predetermined ratio.

15

20. The method of claim 19, wherein x is about 0.75 in the first region and about 0.55 in the second region and y is about 0.25 in the first region and about 0.45 in the second region.

20

21. The method of claim 18, wherein the first region is adjacent the second region with an interface oriented at a predetermined position relative to the laser.

22. The method of any of claims 18-21 further comprising performing
25 said irradiating of a number of different portions of the first and second regions to form a graded ferroelectric sensing member.

23. The method of any of claims 18-21, wherein said irradiating includes scanning a predetermined path along the source with the laser.

30

24. The method of claim 23, wherein said path includes a number of segments each corresponding to a different ratio of the first composition to the second composition.

25. The method of any of claims 18-21, wherein said forming includes depositing the mixture on a substrate.
- 5 26. An oxygen sensor formed by the method of any of claims 18-21.
27. A method of manufacture, comprising:
providing a source of ferroelectric material having a first region with
a first composition and a second region with a second composition different
10 from the first composition;
generating a number of plumes each having a different ratio of the
first composition to the second composition, each of the plumes being
formed from different areas of the first and second regions; and
forming a number of layers each corresponding to a different one of
15 the plumes, the layers each having the different ratio of the first
composition to the second composition to provide a ferroelectric device
with a predetermined compositional gradient.
28. The method of claim 27, wherein the source is a solid composed of
20 $\text{PbZr}_x\text{Ti}_y\text{O}_3$; where x and y have a first predetermined ratio in the first region
and a second predetermined ratio in the second region, the first
predetermined ratio being different from the second predetermined ratio.
29. The method of claim 28, wherein x is about 0.75 in the first region
25 and about 0.55 in the second region and y is about 0.25 in the first region
and about 0.45 in the second region.
30. The method of claim 27, wherein the first region is adjacent the
second region with an interface oriented at a predetermined position
30 relative to a device for performing said generating.

31. The method of any of claims 27-30, wherein said generating the plumes includes irradiating a corresponding number of different portions of the first and second regions.
- 5 32. The method of any of claims 27-30, wherein said irradiating includes scanning across a predetermined path along the source with a laser.
33. The method of claim 32, wherein said path includes a number of segments each corresponding to a different one of the plumes.
- 10 34. The method of any of claims 27-30, wherein said forming includes depositing material from a first one of the plumes on a substrate.
35. An oxygen sensor formed by the method of any of claims 27-30.
- 15 36. An apparatus comprising an oxygen sensor including a PZT ferroelectric sensing member.
37. The apparatus of claim 36 wherein said sensing member is
- 20 comprised of a graded ferroelectric material.
38. The apparatus of claim 36 wherein the said sensor includes at least two metallic electrodes.
- 25 39. The apparatus of claim 38 wherein said electrodes are formed from a material selected from platinum, silver, gold, metal phthalocyanine, and conductive metal oxide.
40. The apparatus of claim 36 and further comprising a circuit
- 30 electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member.

41. The apparatus of any of claims 36-40, wherein a ratio between two compositional constituents increases along a predetermined direction through said sensing member to provide a corresponding compositional gradient.
- 5 42. The apparatus of claim 41, wherein said gradient is established by a number of differently composed layers.
43. The apparatus of claim 41 or 42, wherein said two compositional constituents are zirconia and titania.
- 10 44. The apparatus of any of claims 36-40 wherein said sensing member is formed of $\text{PbZr}_x\text{Ti}_y\text{O}_3$; wherein x is in a range of about 0.5 to about 0.8 and y is in a range of about 0.2 to about 0.5.
- 15 45. The apparatus of claim 44 wherein x is in a range of about 0.55 to about 0.75 and y is in a range of about 0.25 to about 0.45.
46. A method of use, comprising detecting oxygen in an intake or exhaust stream of a vehicle with the apparatus of any of claims 36-40.
- 20 47. A combination, comprising:
a nonstoichiometric metal oxide sensing member to detect oxygen;
and
25 a circuit electrically coupled to said sensing member operable to apply a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm .
48. A combination, comprising:
30 providing a nonstoichiometric metal oxide sensing member;
applying a time varying electric field to said sensing member having a peak magnitude of at least about 1 volt per μm ; and
sensing oxygen with said sensing member during said applying.

49. The combination of claim 47 or 48, wherein said peak magnitude is in a range of about 1 volt per μm to about 1000 volts per μm .

5 50. The combination of claim 49, wherein said peak magnitude is in a range of about 10 volts per μm to about 100 volts per μm .

51. The combination of claim 47 or 48 wherein said sensing member is comprised of a ferroelectric material.

10

52. The combination of claim 47 or 48, wherein said sensing member is comprised of a PZT material.

53. The combination of claim 47 or 48, wherein the system is operable
15 to detect oxygen concentration at a temperature below about 400K.

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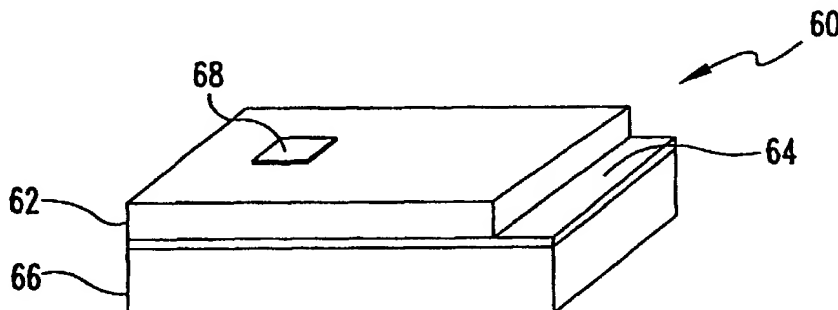
(51) International Patent Classification ⁶ : G01N 27/00, 33/00		A1	(11) International Publication Number: WO 00/07001
			(43) International Publication Date: 10 February 2000 (10.02.00)
(21) International Application Number: PCT/US99/17422		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 30 July 1999 (30.07.99)			
(30) Priority Data: 60/094,721 30 July 1998 (30.07.98) US 60/123,819 11 March 1999 (11.03.99) US			
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(72) Inventors; and (75) Inventors/Applicants (for US only): MANSOUR, Said [US/US]; 2818 Cambridge Street, West Lafayette, IN 47906 (US). BRAZIER, Mark [US/US]; 3037 Courthouse Dr. #1, West Lafayette, IN 47906 (US). MCELFRESH, Michael [US/US]; 931 Princess Drive, West Lafayette, IN 47906 (US).			
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		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: LOW TEMPERATURE OXYGEN GAS SENSOR

(57) Abstract

A highly sensitive oxygen gas sensor (60), which operates at ambient and sub-ambient temperatures was developed using nonstoichiometric metal oxides such as ferroelectric PZT materials or yttria stabilized zirconia. The sensor is constructed of a solid state electrolyte thin film (62) of the nonstoichiometric metal oxide material sandwiched between two metal electrodes (64, 68). An

offset d.c. voltage, which is manifested as a translation of the ferroelectric hysteresis loop, develops between the two electrodes (64, 68) when an electric field is applied. The magnitude and direction of the offset voltage depends on variations in oxygen concentration or partial pressure at one of the device electrodes.



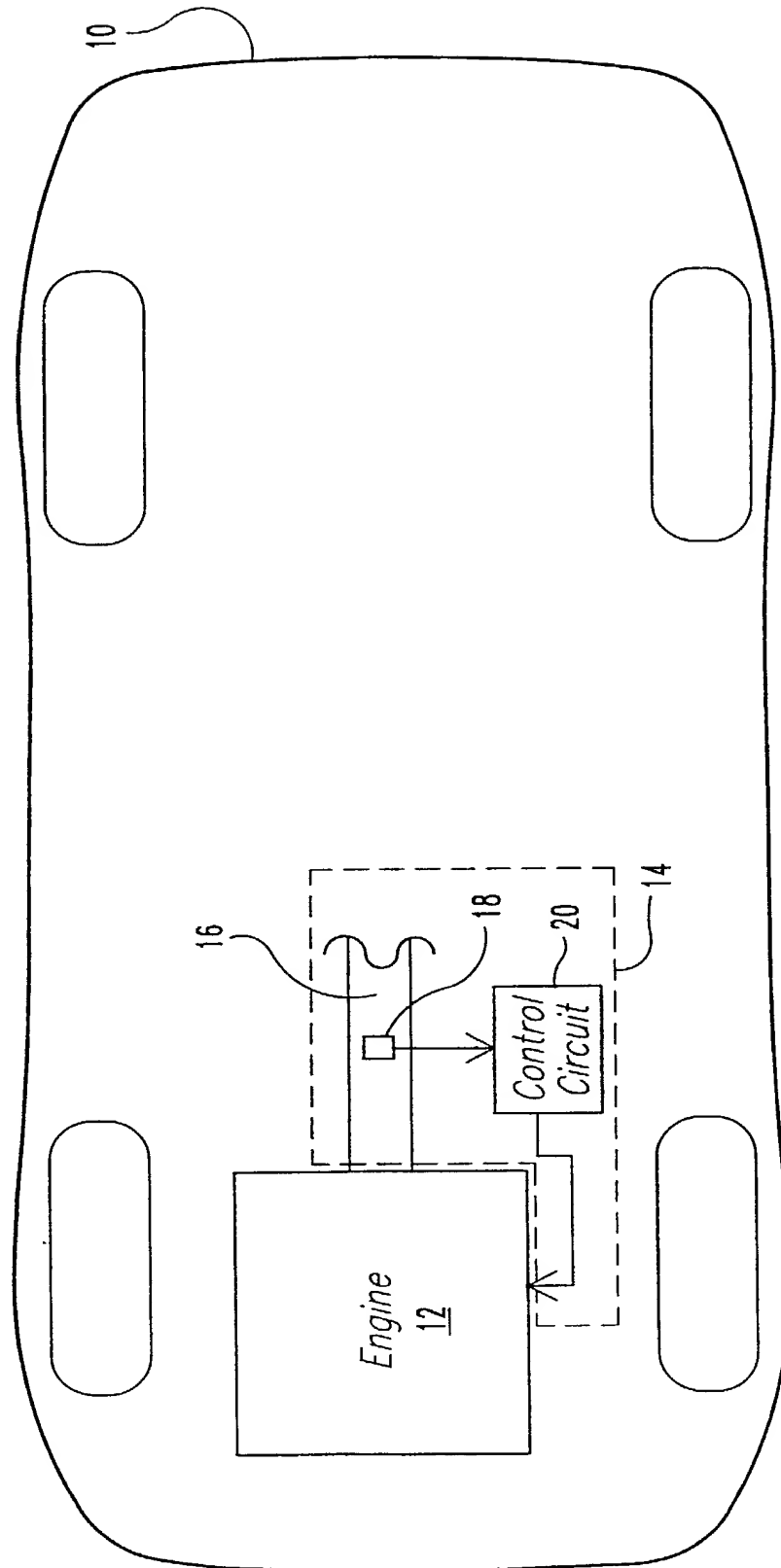


Fig. 1

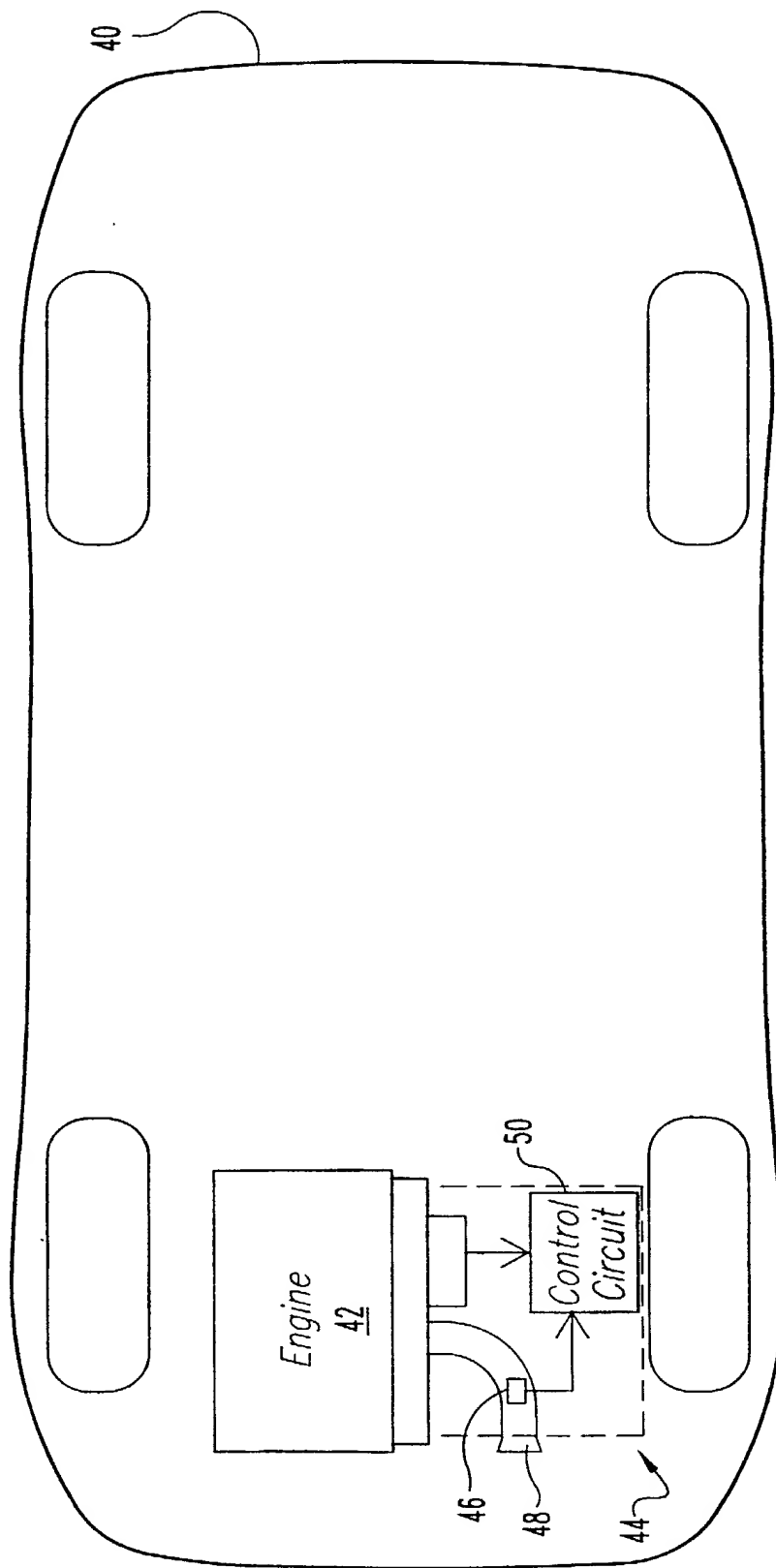


Fig. 2

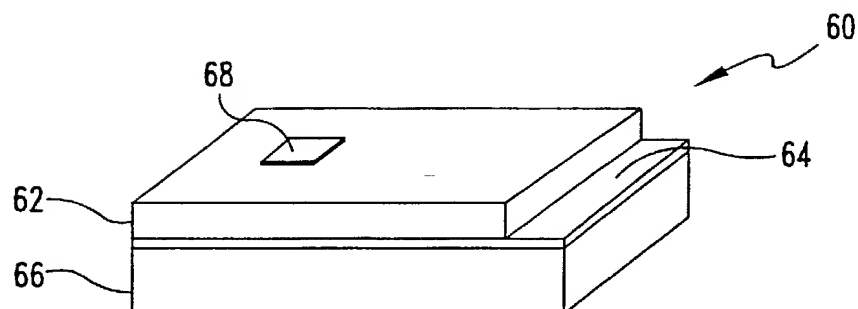


Fig. 3

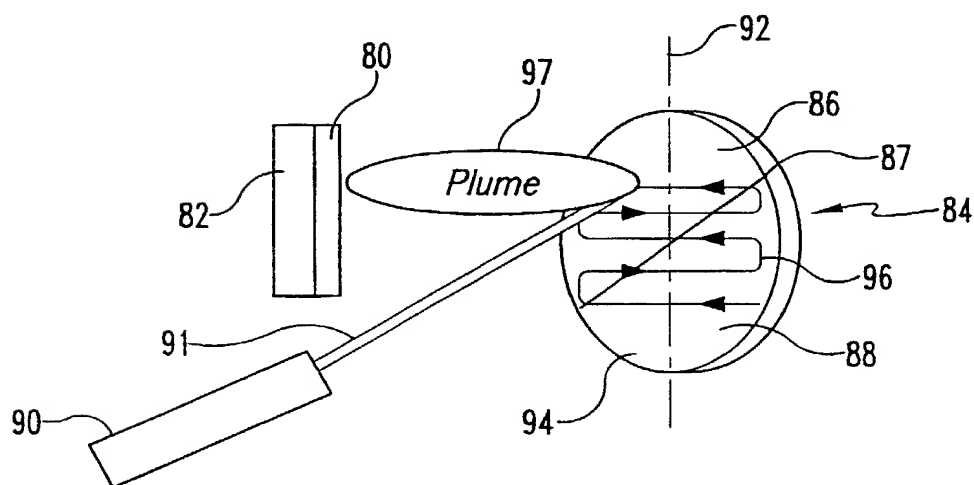


Fig. 4



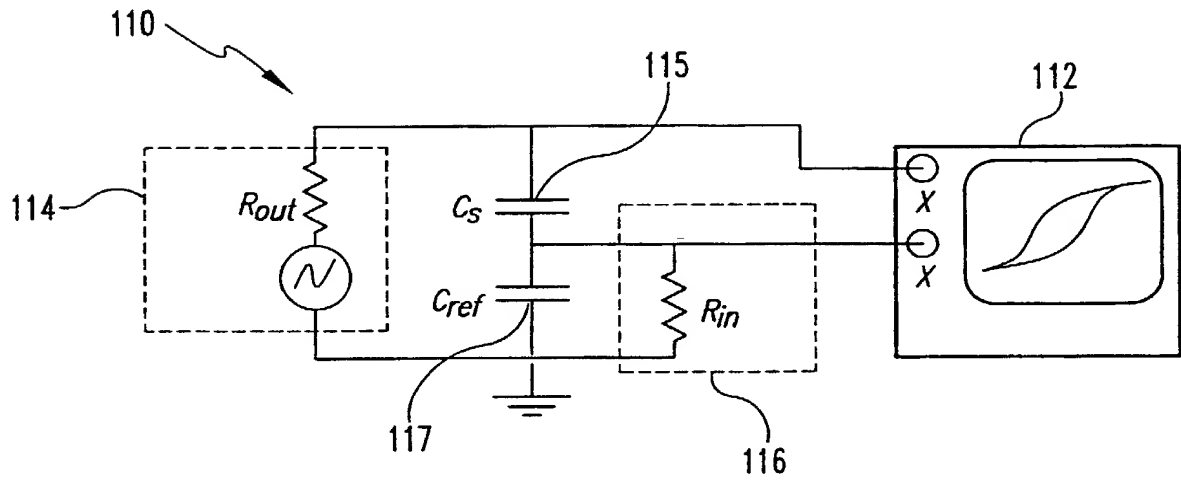


Fig. 7

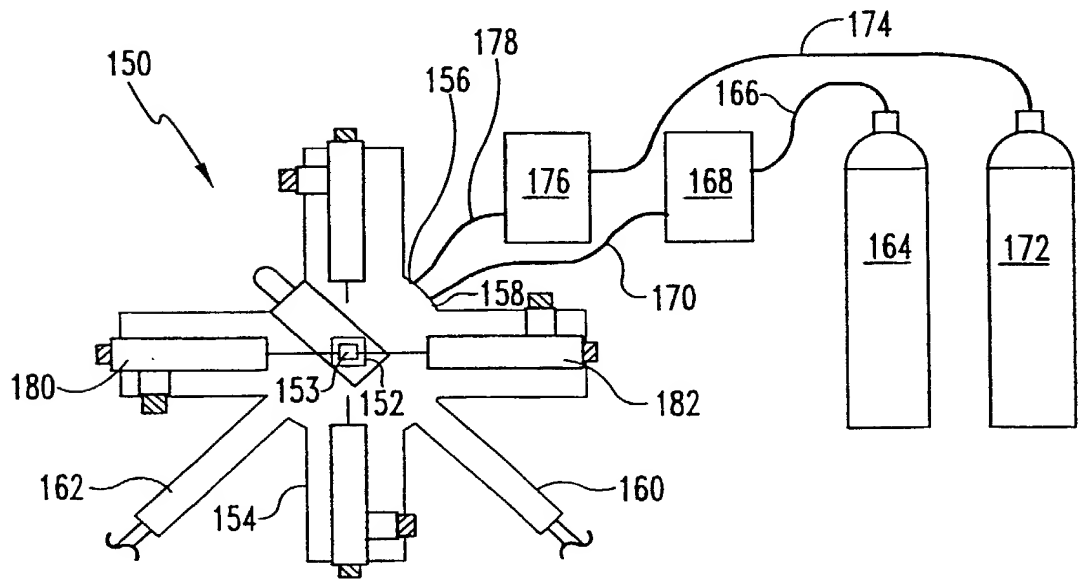
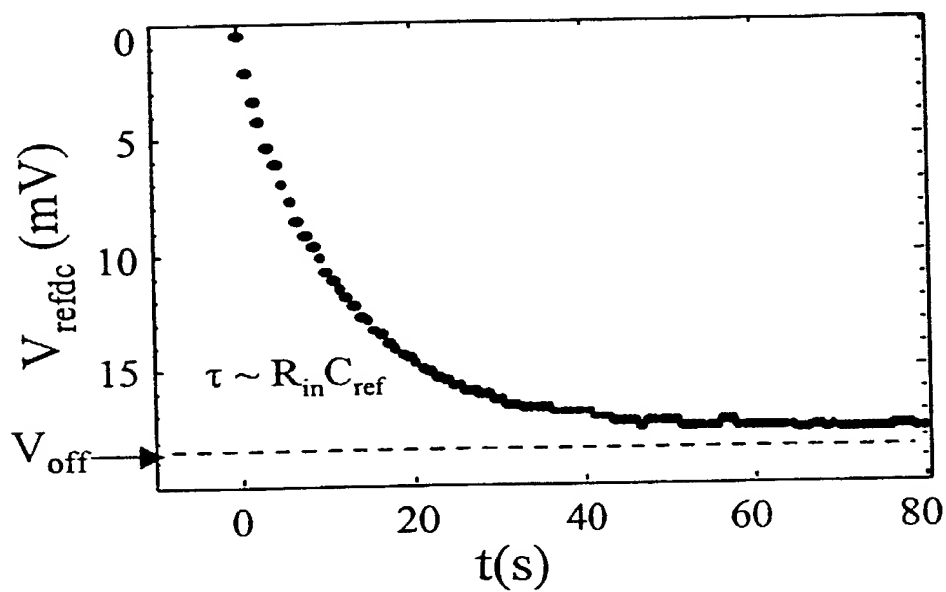
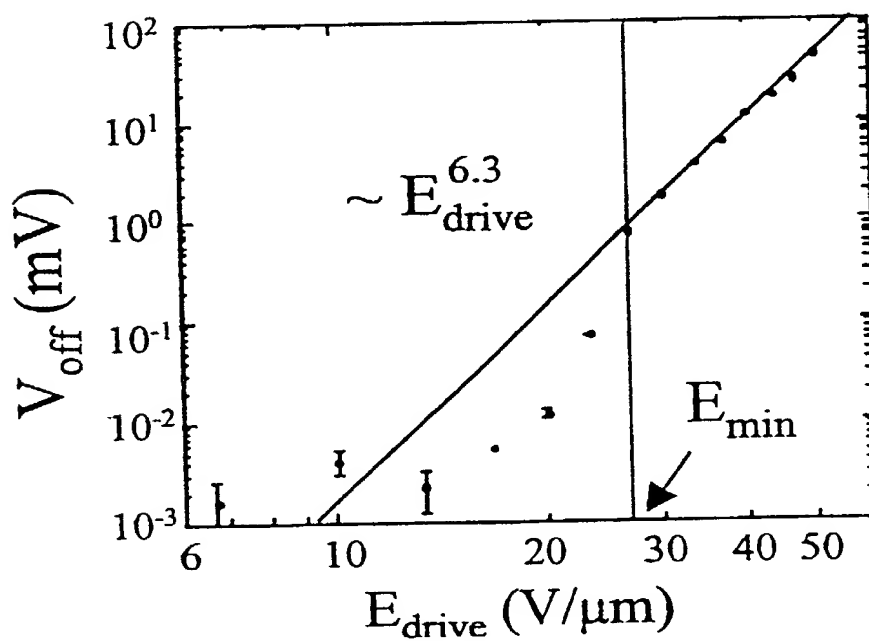


Fig. 8

**Fig. 9a****Fig. 9b**

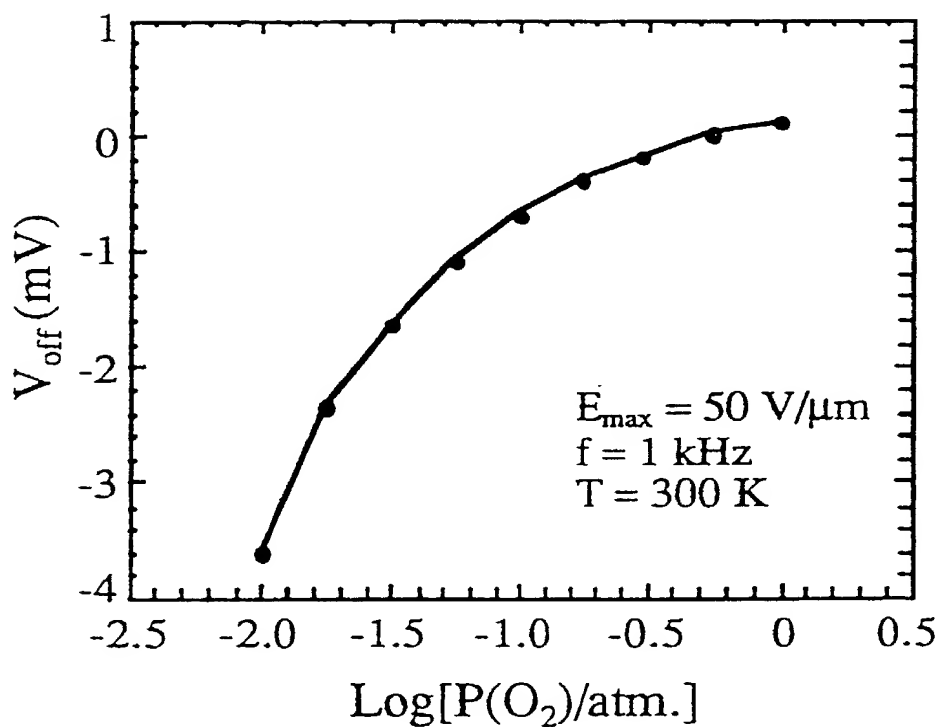


Fig. 10a

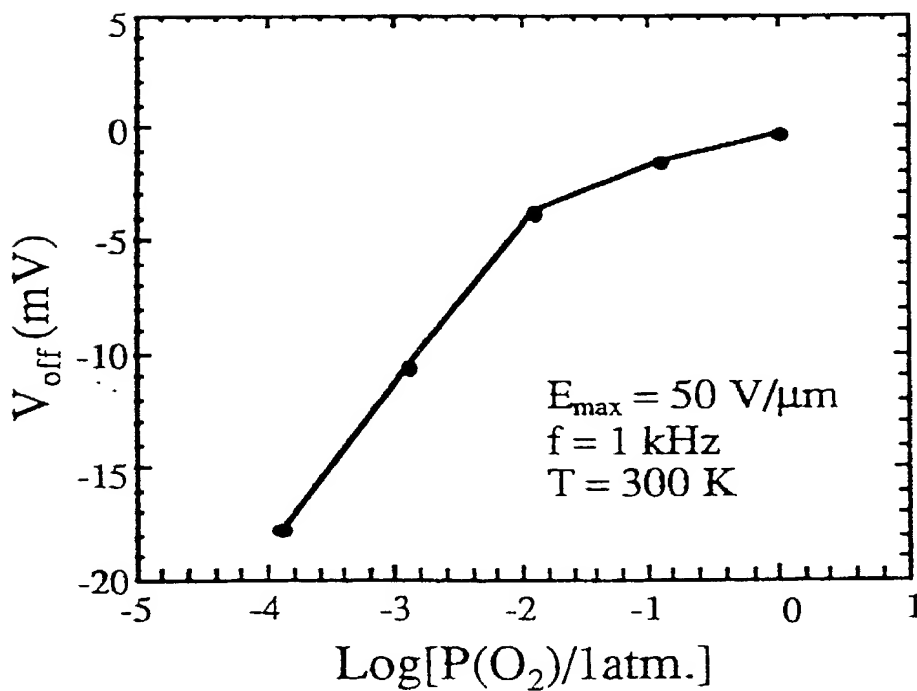


Fig. 10b

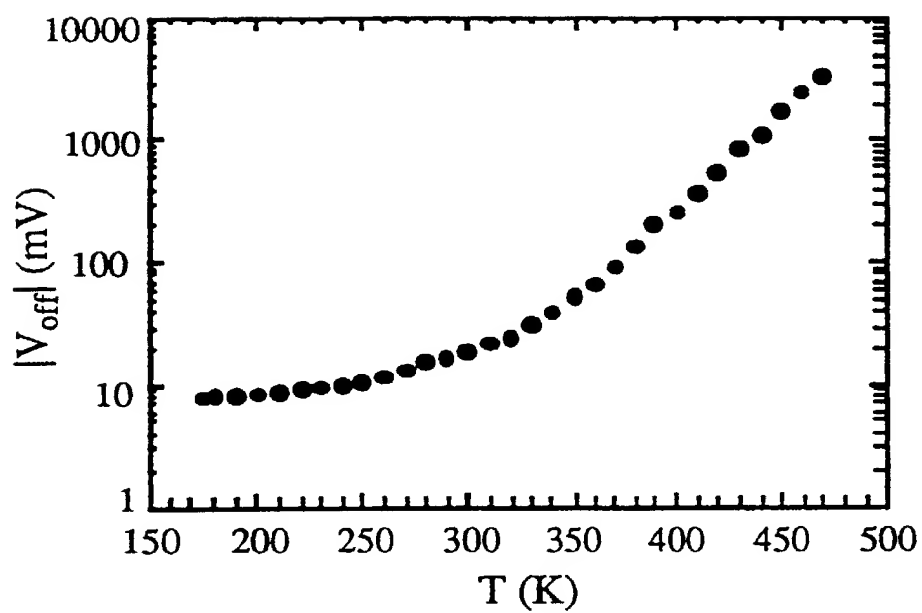
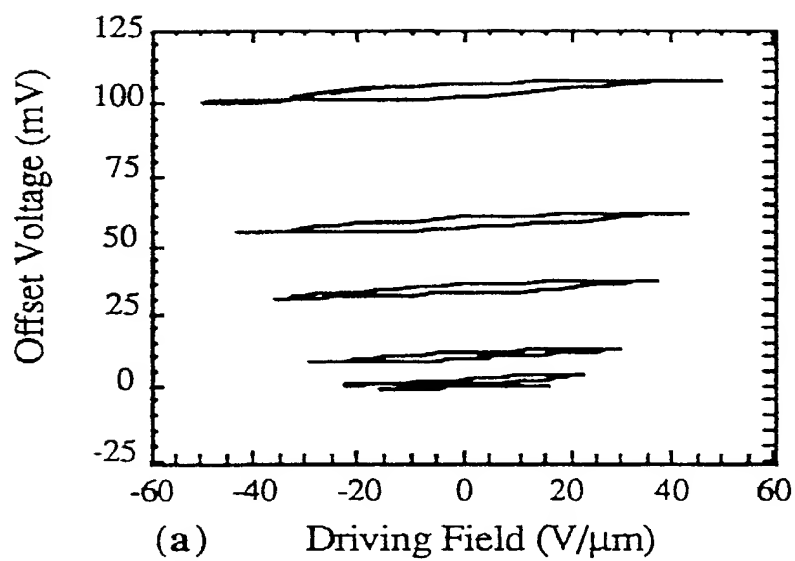
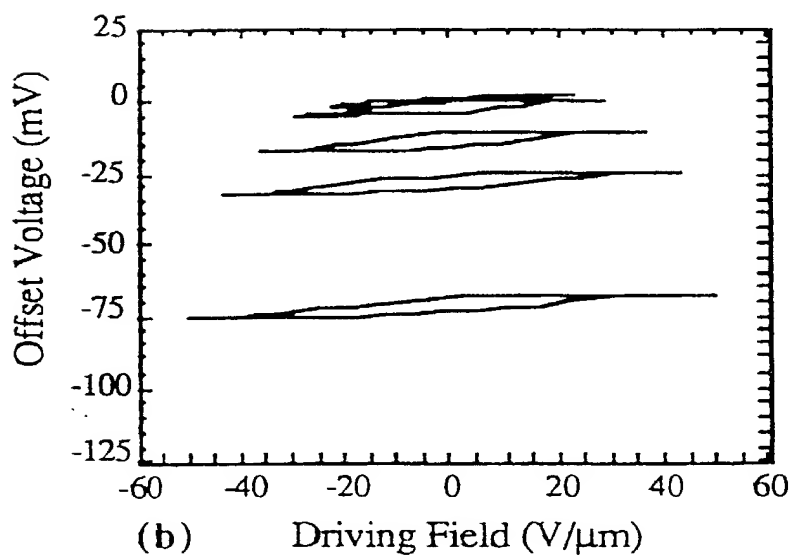
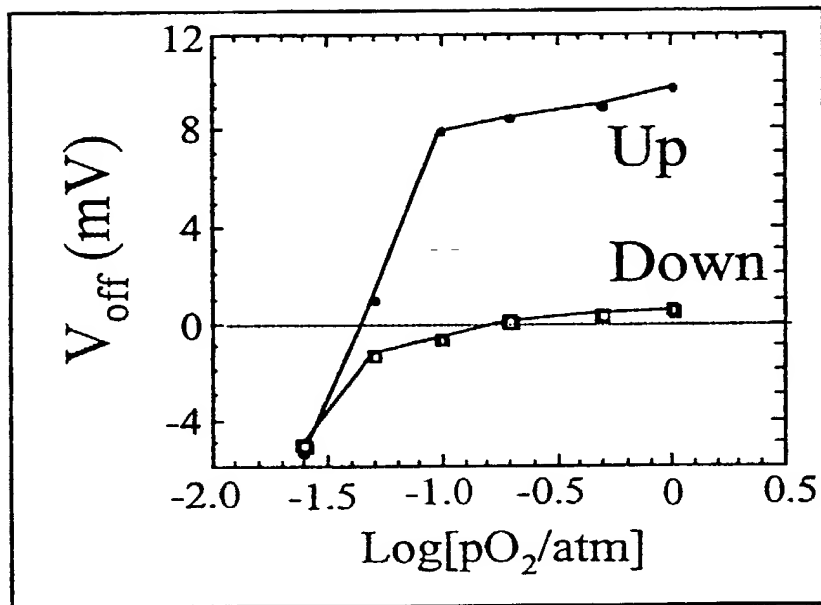
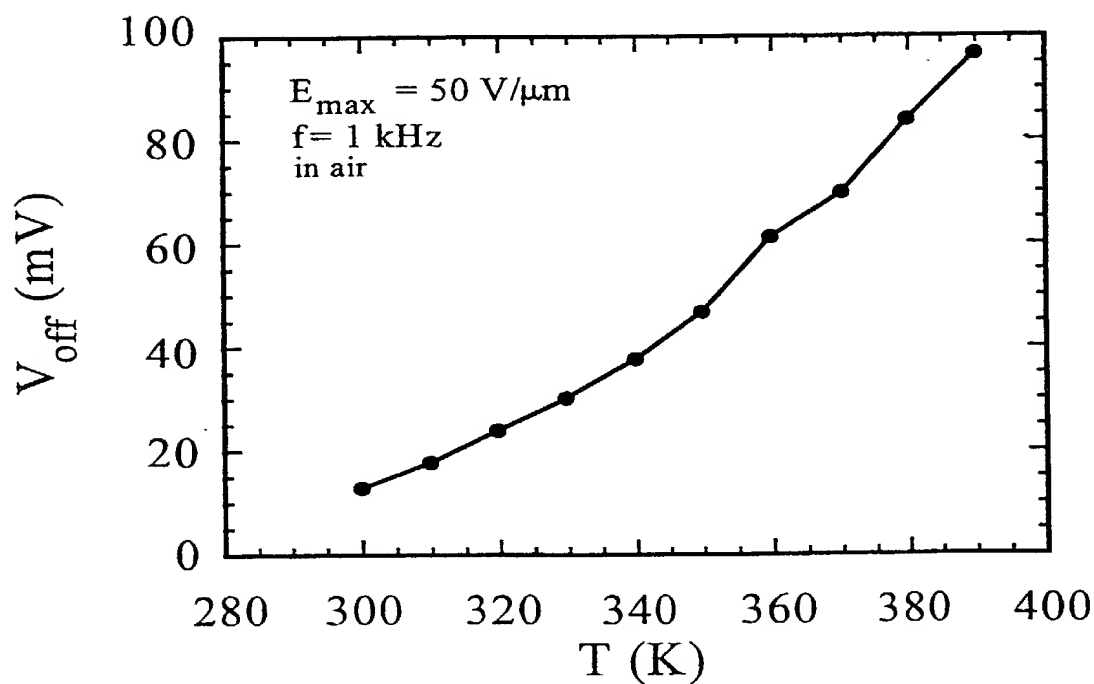
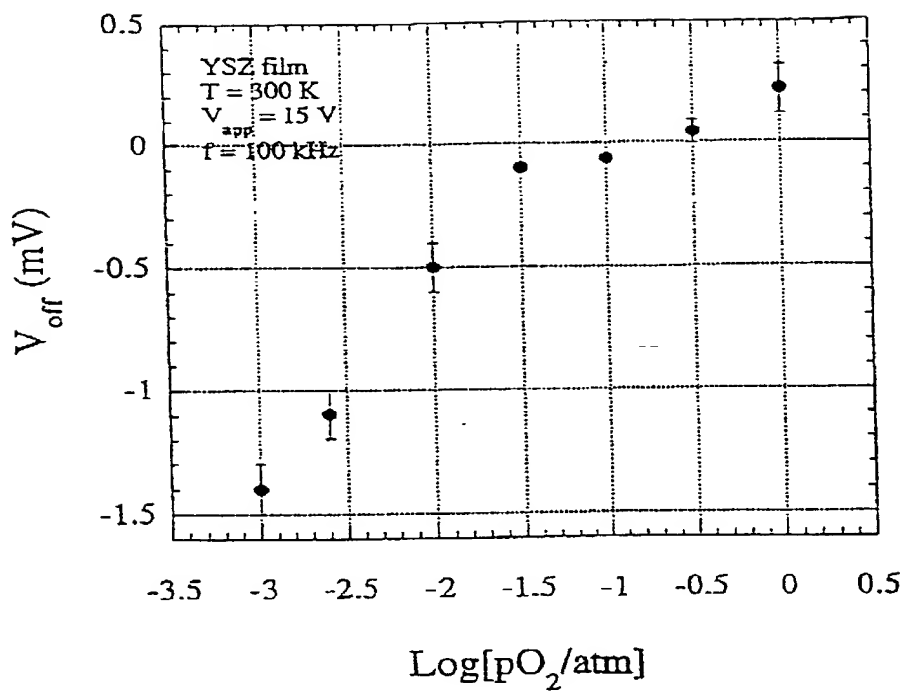
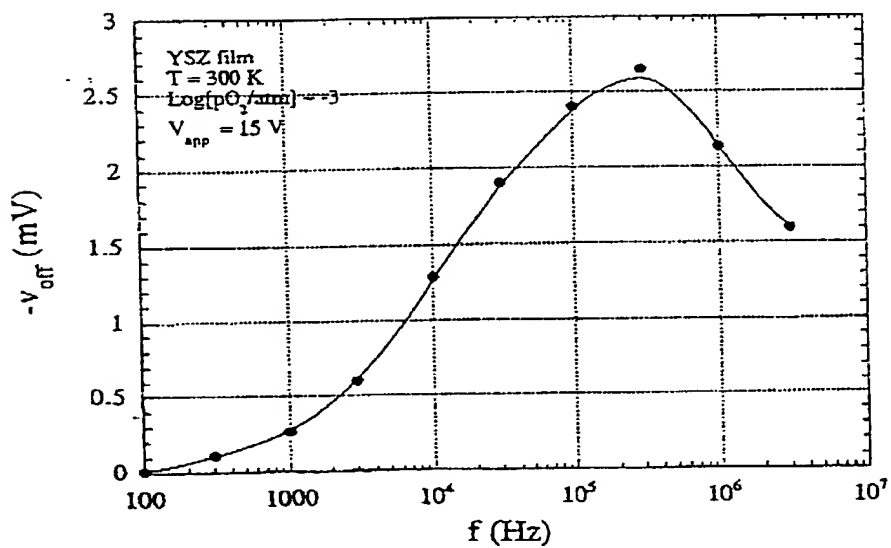


Fig. 10c

09/744793

**Fig. 11a****Fig. 11b**

**Fig. 12****Fig. 13**

**Fig. 14****Fig. 15**

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	First Named Inventor	Said MANSOUR
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I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

LOW TEMPERATURE OXYGEN GAS SENSOR

(Title of the invention)

the specification of which

☐ is attached hereto
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☒ was filed on (MM/DD/YYYY)

07/30/1999

as United States Application Number or PCT International

Application Number

PCT/US99/17422

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03/13/2000

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I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

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60/123,819	03/11/1999	

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☐ A petition has been filed for this unsigned inventor

Given Name

(first and middle (if any)) Said

Family Name

or Surname MANSOURInventor's
Signature [Signature]Date 3/26/01Residence: City West LafayetteState INCountry USCitizenship USMailing Address 2918 Cambridge StreetMailing Address West Lafayette, Indiana 47906 USCity West LafayetteState INZIP 47906Country US

NAME OF SECOND INVENTOR:

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Date

Residence: City West LafayetteState INCountry USCitizenship USMailing Address 3037 Courthouse Drive, #1Mailing Address West Lafayette, Indiana 47906 USCity West LafayetteState INZIP 47906Country US☒ Additional inventors are being named on the 1 supplemental Additional Inventor(s) sheet(s) PTO/SB/02A attached hereto.

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Michael		MCELFRESH	
Inventor's Signature		Date	
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Mailing Address West Lafayette, Indiana 47906 US			
City West Lafayette	State IN	ZIP 47906	Country US
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LOW TEMPERATURE OXYGEN GAS SENSOR

(Title of the Invention)

the specification of which

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Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
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			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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City Indianapolis

State IN

ZIP 46204

Country US

Telephone 317-634-3456

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NAME OF SOLE OR FIRST INVENTOR:

☐ A petition has been filed for this unsigned inventorGiven Name
(first and middle (if any)) SaidFamily Name
or Surname MANSOURInventor's
Signature

Date

Residence: City West Lafayette

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Country US

Citizenship US

Mailing Address 2818 Cambridge Street

Mailing Address West Lafayette, Indiana 47906 US

City West Lafayette

State IN

ZIP 47906

Country US

NAME OF SECOND INVENTOR:

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Date

Residence: City West Lafayette

State IN

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Given Name (first and middle (if any))		Family Name or Surname		
Michael		MCELFRESH		
Inventor's Signature 		Date 3/20/01		
Residence: City	West Lafayette	State	IN	
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Citizenship	US			
Mailing Address 931 Princess Drive				
Mailing Address West Lafayette, Indiana 47906 US				
City	West Lafayette	State	IN	
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Name of Additional Joint Inventor, if any:		<input type="checkbox"/> A petition has been filed for this unsigned inventor		
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Spiro Bereveskos	#30,821		
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of:)
 Said Mansour et al.)
 Serial No. 09/486,301)
 I.A. Filing Date: 30 July 1999)
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Applicants qualify as a small entity. The statutory fee of \$55.00 for a small entity for this request is enclosed herewith. The Patent and Trademark Office is authorized to charge any deficiency or apply any overpayment credit to Deposit Account No. 23-3030, but not to include the payment of any issue fees that are or may become due.

Respectfully submitted,

By: James B. Myers Jr.
 James B. Myers Jr., Reg. No. 42,021
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Adjustment date: 05/21/2002 MALI11
 04726/2001 NGUYEN 00000166 09486301
 01 FC:215 -55.00 DP

05/21/2002 MALI11 00000131 09744793
 01 FC:215 55.00 DP

EXHIBIT

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REQUEST FOR EXTENSION OF TIME

JCO Rec'd OCT/PTO

25 APR 2001
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of:)
 Said Mansour et al.)
 Serial No. ~~09/486,301~~ 09/744,793)
 I.A. Filing Date: 30 July 1999)
 LOW TEMPERATURE OXYGEN GAS SENSOR)

I hereby certify that this correspondence is
 being deposited with the United States
 Postal Service as first class mail in an
 envelope addressed to the Assistant
 Commissioner for Patents, Washington,
 D C 20231 on
 April 23, 2001

(Date of Deposit)

James B. Myers Jr.

Name of Registered Representative

Signature

April 23, 2001

Date of Signature

REQUEST FOR EXTENSION OF TIME

Hon. Commissioner for Patents
 Washington, D.C. 20231

Sir:

Applicants' attorney requests that the date for responding to the Notification of Missing Requirements dated 27 February 2001 be extended one month, to and including 27 April 2001.

Applicants qualify as a small entity. The statutory fee of \$55.00 for a small entity for this request is enclosed herewith. The Patent and Trademark Office is authorized to charge any deficiency or apply any overpayment credit to Deposit Account No. 23-3030, but not to include the payment of any issue fees that are or may become due.

Respectfully submitted,

By: James B. Myers Jr.
 James B. Myers Jr., Reg. No. 42,021

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